attached separately via two BNC connectors to the base of the probe. A General Radio 1164-A frequency synthesizer, locked to a 5-MHz source from the spectrometer, and an RF Communications Inc. Type 805 amplifier were used to decouple ^{11}B. Facility for proton decoupling was already available with the instrument.

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Registry No. $Zr(BH_4)_4$, 12370-59-1.

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Base Hydrolysis of Resolved Halogeno- and Azido[2,6-bis(aminomethyl)pyridine](1,3-diamino-2-propanol-*N*,*N'*)cobalt(III) Ions. The Question of π Stabilization in the S_N1cB Mechanism

URSULA TINNER and WERNER MARTY*[1]

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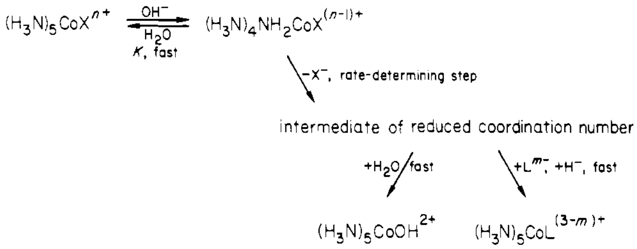
Some new optically active Co(III) pentaamine complexes have been synthesized that are specifically designed to test whether in the base hydrolysis reaction a trigonal bipyramid or a square pyramid is the preferred intermediate state following loss of the leaving group. In these species, a prochiral bidentate ligand is used to see whether its unique symmetry plane coincides with a plane of symmetry in the intermediate. Such coincidence is anticipated if the intermediate is a π-stabilized trigonal bipyramid. $[Co(bamp)(dapo)X]^{2+}$ ions (bamp = 2,6-bis(aminomethyl)pyridine, dapo = 1,3-diamino-2-propanol, X = Cl^-, Br^-, N_3^-) were resolved with use of dibenzoyltartaric acid. Their optical purity (≥97%) was established by interrelating independently resolved species by known stereoretentive reactions. Base hydrolysis (X = Cl^-, $k_{OH} = 2.9 \times 10^3$ dm^3 mol^{-1} s^{-1}; X = Br^-, $k_{OH} = 1.6 \times 10^4$ dm^3 mol^{-1} s^{-1}; 25 °C, $\mu = 1.0$) occurs with full retention of configuration at Co(III). In N_3^- solution (1 mol dm^{-3}), the base hydrolysis reaction produces ~4% azido complex from the chloro and bromo complexes. $[2p(N)\rightarrow 3d_{x^2-y^2}(Co)]$ π stabilization is not considered significant in the intermediate state after loss of the leaving group; certainly its lifetime is not appreciably lengthened by such bonding. This result is attributed to the inability of pyridine π orbitals to give significant bonding. The possibility of $[3d_{xy}(Co)\rightarrow\pi^*(pyridine)]$ back-bonding in stabilizing a square-pyramidal intermediate state is discussed.

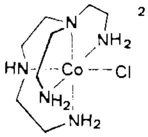
Introduction

The base hydrolysis of Co(III) amine complexes is the object of extensive study,[2-4] and Scheme I shows a currently widely accepted mechanism. The proposal of a short-lived intermediate of reduced coordination number is based on stereochemical criteria,[5] on the results of competition experiments,[5,6] and on the observation of steric acceleration by increasingly bulky alkylamine ligands.[7] More recently, however, similar stereochemical[8,9] and competition studies,[8-10] carried out over an extended range of pentaamine structures and differently charged leaving groups, revealed some leaving-group dependence of the substitution process, which was rationalized in terms of an I_d mechanism.

A classical hypothesis interprets the accelerated loss of the leaving group from the deprotonated reactant as the consequence of π-orbital overlap of the type $[2p(\text{deprotonated nitrogen})\rightarrow 3d_{x^2-y^2}(Co(III))]$.[11] This model predicts that stabilization from this source will develop as the leaving group is being removed and it will reach its maximum in the five-coordinate intermediate if its configuration is trigonal bipyramidal and if the deprotonated nitrogen adopts a planar configuration with the nodal plane of its 2p orbital acting as a symmetry plane of the molecule. This proposal has been used to interpret the stereochemical course of various base hydrolysis reactions[12] and recently to rationalize the base hydrolysis reactivity pattern of chloropentaamine complexes.[13] On the other hand, the base hydrolysis reaction of $[Co(sym\text{-}trenen)Cl]^{2+}$ gave no evidence for a planar configuration of the secondary amine nitrogen, which is considered to be deprotonated in the reactive conjugate base.[14] While this ex-

Scheme I. The Proposed S_N1cB Mechanism for Co(III) Pentaamine Base Hydrolysis[4-6]





$[Co(sym\text{-}trenen)Cl]^{2+}$

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[1] To whom correspondence should be addressed at the Université de Neuchâtel.

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periment was designed to examine the stereochemical consequences of the π-stabilization model at the deprotonated nitrogen center, other tests may focus on the simultaneous stereochemical consequences at the Co(III) center. Such tests require judicious choice of a suitable ligand system, and this paper records one of our attempts in this direction.

Experimental Section

Materials. bamp·3HCl was prepared as described.[15] dapo (practical grade, ≥95%) and dibenzoyl-D- and -L-tartaric acids (purum, ≥98%) were used as purchased (Fluka AG, Buchs, Switzerland). All other reagents and solvents were of analytical or purissimum grade.

Physical Measurements. UV–vis spectra and the slower kinetics runs were measured on a Cary 14 spectrophotometer. A Lauda thermostat maintained the cell compartment at 25.0 ± 0.1 °C. Stopped-flow kinetics were followed on a Durrum instrument at 25.0 ± 0.2 °C. ^1H and ^{13}C NMR spectra were recorded on a Bruker HX 90-E instrument at 25 °C in the FT mode or on a Bruker HX 360 instrument for ^1H NMR spectra at 360 MHz. A JASCO J40 instrument was used for CD measurements (in 0.1 mol dm^{-3} $HClO_4$ if not stated otherwise).

Preparations. (±)-(*OC*-6-33)-Chloro(1,3-diamino-2-propanol-*N*,*N'*)(2,6-pyridinebis(methanamine)-*N*,*N'*,*N''*)cobalt Diperchlorate (1-$(ClO_4)_2$). To a stirred solution of $CoCl_2·6H_2O$ (36.1 g, 0.15 mol) and $NaClO_4·H_2O$ (33.3 g) in methanol (130 mL) was added dropwise within 3 h a solution of bamp·3HCl (26.1 g, 0.11 mol), NaOH (4.6 g, 0.12 mol) and dapo (15 g, 0.17 mol) in methanol (500 mL). A stream of oxygen was then passed through the solution for 20 min. Some Co(III) hexaamines were filtered off, and adhering chloropentaamine was extracted from them with methanol. The combined red filtrates were evaporated to dryness. The residue was recrystallized from 0.1 mol dm^{-3} perchloric acid containing sodium perchlorate at 60 °C; yield 22.7 g (40%). *Warning*! There is a latent danger of explosion when handling perchlorate salts of cobalt amines.[16] Anal. Calcd for $C_{10}H_{21}Cl_3CoN_5O_9$: C, 23.07; H, 4.07; N, 13.45. Found: C, 22.98; H, 3.96; N, 13.46.

(±)-(*OC*-6-33)-Bromo(1,3-diamino-2-propanol-*N*,*N'*)(2,6-pyridinebis(methanamine)-*N*,*N'*,*N''*)cobalt Tetrabromozincate (2-$ZnBr_4$). A solution of 1-$(ClO_4)_2$ (5 g, 9.6 mmol) was treated with silver nitrate (1.63 g, 9.6 mmol) in water (200 mL) with stirring for 12 h. Silver chloride was filtered off, and the filtrate was treated with hydrobromic acid (48%) and concentrated by evaporation. After 12 h, addition of hydrobromic acid (48%) and zinc bromide precipitated purple 2-$ZnBr_4$; yield 6.5 g (90%). Anal. Calcd for $C_{10}H_{21}Br_5CoN_5OZn$: C, 15.99; H, 2.82; N, 9.32. Found: C, 16.07; H, 2.84; N, 9.22.

(±)-(*OC*-6-33)-Azido(1,3-diamino-2-propanol-*N*,*N'*)(2,6-pyridinebis(methanamine)-*N*,*N'*,*N''*)cobalt Tetrachlorozincate (3-$ZnCl_4$). Sodium azide (15 g) was added to a solution of 1-$(ClO_4)_2$ (5 g, 9.6 mmol) in acetic acid (0.2 mol dm^{-3}, 85 mL). The solution was heated to 80 °C until the brown-red color of **3** had developed. The solution was then poured into isopropyl alcohol–methanol (3:2, 250 mL) containing zinc chloride (15 g) and hydrochloric acid (37%, 2 mL). On cooling, red crystals formed, and crystallization was completed by adding isopropyl alcohol (200 mL) containing zinc chloride (20 g); yield 4.1 g (80%). Anal. Calcd for $C_{10}H_{21}Cl_4CoN_8Zn$: C, 22.43; H, 3.95; N, 20.93. Found: C, 22.32; H, 3.89; N, 20.82.

Resolution of (±)-1. The racemic perchlorate (5 g, 9.6 mmol) was dissolved in water (60 mL) containing lithium chloride (2.5 g) and ethanol (50 mL). Dibenzoyl-L-tartaric acid ($[\alpha]^{20}_{546}$ = −134°, 3.6 g, 9.6 mmol) was then added with stirring. Stirring was continued for 20 min at 0 °C, and the less soluble dibenzoyltartrate diastereoisomer was filtered off. It was suspended in ethanol and dissolved by adding the minimal amount of perchloric acid (0.1 mol dm^{-3}). Addition of lithium perchlorate to the cooled solution (0 °C) precipitated $(-)_{578}$-1-$(ClO_4)_2$. $(+)_{578}$-1-$(ClO_4)_2$ was recovered from the mother liquor. This precipitation procedure with dibenzoyl-L-tartaric acid ($(-)_{578}$ antipode) and dibenzoyl-D-tartaric acid ($(+)_{578}$ antipode) followed by recovery of the corresponding perchlorates was repeated 3–4 times until constant ellipticity was reached ($[\theta]^{20}_{546}$ = −825, $[\theta]^{20}_{546}$ = +807; combined yield of the two antipodes 74%). The visible spectra of the resolved perchlorates fully agreed with that of the racemate. The composition of the diastereoisomeric salts is very complex and was not determined.

Resolution of (±)-2. The racemic tetrabromozincate (4.46 g, 5.9 mmol) was dissolved in aqueous lithium bromide (130 mL, 1 mol dm^{-3}) and ethanol (100 mL). Dibenzoyl-L-tartaric acid (2.23 g, 5.9 mmol) was added with stirring at 0 °C. After 20 min, the precipitated diastereoisomer was filtered off. From the filtrate, incompletely resolved $(+)_{578}$-2-$ZnBr_4$ was crystallized by adding 48% hydrobromic acid and zinc bromide. The less soluble diastereoisomer was suspended in ethanol and dissolved in the minimum of hydrobromic acid (0.2 mol dm^{-3}). From this solution, $(-)_{578}$-2-$ZnBr_4$ was crystallized as above. Repeating these operations three times gave a product of constant ellipticity ($[\theta]^{20}_{560}$ = −782); yield 78%. The visible spectrum of this sample fully agreed with that of the racemate. The diastereoisomeric dibenzoyl-L-tartrate had a complex composition, which was not determined.

Resolution of (±)-3. $(-)_{578}$-1-$(ClO_4)_2$ (180 mg, 0.3 mmol, $[\theta]^{20}_{546}$ = −615, 74.5% optically pure) was treated with sodium azide as described for (±)-**3**. The cooled solution of the azido complex was poured into methanol–lithium bromide. $(-)_{578}$-3-Br_2 crystallized slowly at 0 °C. The solid was washed with isopropyl alcohol and ether and dried; yield 110 mg, 65%. A sample of this preparation ($[\theta]^{20}_{508}$ = −992) was nitrosated (see below) to give the aqua ion **4** ($[\theta]^{20}_{530}$ = −1033, 89.4% optically pure) indicating improved optical purity of $(-)_{578}$-**3** as a consequence of the crystallization of the bromide salt. In another experiment, supposedly optically pure $(-)_{578}$-1-$(ClO_4)_2$ with maximum ellipticity (see above) was converted into 3-Br_2 by the same procedure. The resulting azido complex was again nitrosated to give $(-)_{578}$-**4** with $[\theta]^{20}_{508}$ = −1155 (97% of the highest ellipticity recorded for **4**, i.e., the optical purity remained the same within the error, which is consistent with complete resolution of **1** and **3**).

Stereochemical Reaction Cycles. The Hg^{2+}-induced aquations of optically pure **1** and **2** were carried out by adding a sample of solid $Hg(NO_3)_2·0.5H_2O$ to a solution of the complex in perchloric acid (0.1 mol dm^{-3}).

Optically pure **3** was nitrosated in perchloric acid (0.1 mol dm^{-3}) by adding 10–15% excess of solid sodium nitrite. After ca. 10 min at room temperature, about the same quantity of urea was added to destroy any unreacted NO^+. For the chlorination of **2**, chlorine was passed through a solution of the complex in perchloric acid (0.1 mol dm^{-3}) for 1 min. The solution was then allowed to stand (5 min, 20 °C), and unreacted chlorine was removed by passing a stream of nitrogen through the solution (15 min, 20 °C).

Competition Experiments. In a typical experiment, the complex (**1** or **2**, 30–40 mg) was dissolved in aqueous sodium azide solution (1 mol dm^{-3}, 5 mL, pH 7 ($HClO_4$)). A solution of NaOH (0.4 mol dm^{-3}) in aqueous sodium azide (1 mol dm^{-3}, 5 mL) was added with vigorous stirring. After 60 s, the solution was quenched with perchloric acid (60%, 1 mL), diluted, and sorbed on cation-exchange resin (Dowex 50WX2, 200–400 mesh, H^+ form, 7 × 1 cm). Unreacted azide ion was washed out with water until tests with ferric ion were negative. **2** and **3** were then eluted with perchloric acid (2 mol dm^{-3} for **3** and 3 mol dm^{-3} for **4**) and their visible spectra (and CD spectra when resolved starting materials were used) were recorded immediately after elution. An orange band remained on the top of the column, which could not be eluted by a variety of eluants including 37% HCl. Attempts to elute this species from Sephadex SP-C25 were equally unsuccessful. In addition, the following blank experiments were carried out. A sample of (±)-3-$ZnCl_4$ was treated exactly under the conditions of the competition experiments. After absorption and elution as above 99 ± 1% was recovered. Samples of (±)-**1** and (±)-**2** were base hydrolyzed under the conditions of the competition experiments, including the ion-exchange procedure, except that sodium azide was substituted by $NaClO_4$. Recovery of (±)-**4** was 99 ± 1%. To a solution of (±)-$[Co(bamp)(dapo)OH]^{2+}$ in base (0.4 mol dm^{-3}) was added sodium azide to make up 1 mol dm^{-3}. The mixture was quenched with acid after 60 s and sorbed on an ion-exchange column. Elution gave ≤2% of **3**, and this amount of azido complex formed by subsequent reaction of the hydroxo product with azide ion is included in the data in Table III.

Results

Preparation and Properties of (±)-$[Co(bamp)(dapo)X]^{2+}$ Ions. Dioxygen oxidation of a buffered mixture of bamp·3HCl,

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Table I. UV-Vis and CD Spectra of $[Co(bamp)(dapo)X]^{n+}$ Complexes

compd	UV-vis[a] λ, nm	UV-vis[a] ε, M^{-1} cm^{-1}	CD[b] λ, nm	CD[b] θ, deg mol^{-1} dm^3 mol^{-1}
(1) $(-)_{578}$-$[Co(bamp)(dapo)Cl]^{2+}$			546	−825
	474 (max)	116	508	0
			463	+986
	408 (min)	38		
	360 (max)	123		
	340 (min)	107		
(2) $(-)_{578}$-$[Co(bamp)(dapo)Br]^{2+}$			560	−782
	530 (sh)		517	0
	476 (max)	108	467	+908
	418 (min)	96	403	+249[c]
			382	+329[d]
			346	0
(3) $(-)_{578}$-$[Co(bamp)(dapo)N_3]^{2+}$	485 (max)	321	508	−1155
			519	0
			469	+1914
	428 (min)	124	404	0
(4) $(-)_{578}$-$[Co(bamp)(dapo)OH_2]^{3+}$			530	−1188
			496	0
	462 (max)	132	457	+1330
	398 (min)	34	388	0
			359	−344
	345 (max)	131		
	326 (min)	123		
			318	0

[a] In 0.1 M $HClO_4$; $T = 25$ °C, $Co_t = (2\text{–}3) \times 10^{-3}$ M. [b] In 0.1 M $HClO_4$; $T = 25$ °C, $Co_t = (1\text{–}2) \times 10^{-3}$ M. [c] Minimum. [d] Maximum.

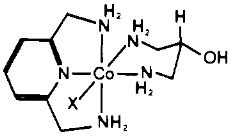

Figure 1. $[Co(bamp)(dapo)X]^{n+}$: **1**, X = Cl^-; **2**, X = Br^-; **3**, X = N_3^-; **4**, X = OH_2.

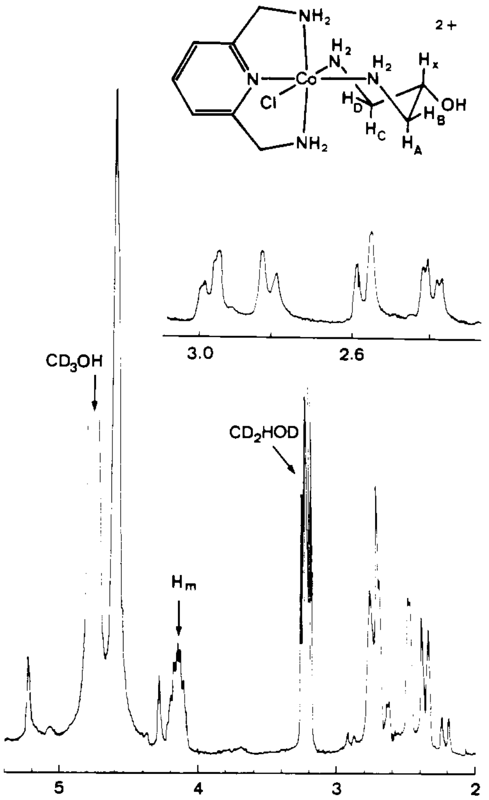

Figure 2. High-field portion of the ^1H NMR spectrum at 90 MHz and 360 MHz (insert). The abscissa is the chemical shift δ relative to TSP internal standard.

dapo, and cobalt(II) chloride in methanol gave the red chloro complex **1** (X = Cl^-), which was isolated as the diperchlorate (bamp = 2,6-bis(aminomethyl)pyridine; dapo = 1,3-diamino-2-propanol; X = Cl^-, Br^-, N_3^- (Figure 1)). This reaction may proceed via a μ-peroxo-decaamine intermediate, but this species was not found to accumulate in appreciable quantities during the reaction. Hexaamine species were major byproducts in this preparation. The $ZnBr_4^{2-}$ salt of cation **2** (X = Br^-) was prepared by Ag^+-assisted aquation of **1** and subsequent treatment with $HBr\text{–}ZnBr_2$. **3** (X = N_3^-) formed on treatment of **1** with NaN_3 in aqueous acetic acid and was isolated as the $ZnCl_4^{2-}$ salt. The visible absorption spectra of **1–3** and of (±)-$[Co(bamp)(dapo)(OH_2)]^{3+}$, **4**, are listed in Table I. The spectrum of **1** closely resembles that of $[Co(bamp)(tmd)Cl]^{2+}$ (tmd = 1,3-diaminopropane) and similar pentaamines,[15] indicating coordination of dapo via the two amine functions. The ^1H NMR spectrum of **1** (Figure 2) shows the pattern of the three pyridine ring protons (δ 8.1–7.4), the methylene protons of bamp (s, δ 4.6), the single proton H_x (m, δ 4.15), and the four methylene protons of dapo (δ 2.9–2.1). The amine protons of dapo are exchanged under the conditions of the recording. The dapo CH_2 pattern is greatly simplified in the 360-MHz spectrum (Figure 2, insert). The methylene groups H_AH_B (lower field) and H_CH_D (higher field) are now well separated, and the geminal couplings J_{AB} and J_{CD} as well as the vicinal trans couplings J_{AX} and J_{CX} are identical (4 and 13.6 Hz, respectively). The lower field CH_2 pattern is broadened by incomplete exchange of the adjacent NH protons (irradiation at the broad cis-NH_2 signal appearing at 5.4 ppm in acid solution sharpens this pattern). As it is known that exchange of NH_2 protons trans to Cl is faster than cis to Cl in Co(III) chloro pentaamines,[5,14] the observed broadening of the CH_2 pattern supports the assignment given on the basis of chemical shifts.[17] The ^{13}C NMR spectrum of **1** shows the bamp carbon atoms at the previously observed chemical shifts.[15] Three more resonances arise from the dapo

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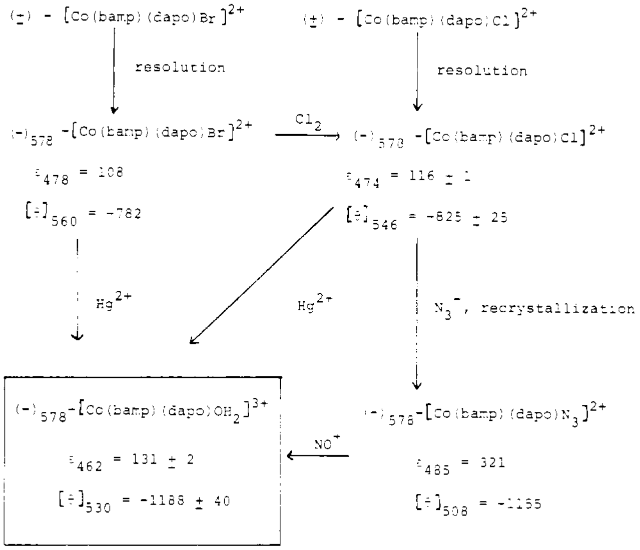
[17] Yoneda, H.; Nakashima, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 669.

Scheme II. Stereochemical Correlations between Resolved $[Co(bamp)(dapo)X]^{n+}$ Ions[a]



[a] $[\theta]^{25}_{\lambda}$ is given in units of deg mol^{-1} dm^3 m^{-1}.

carbons: 63.8 ppm (OH-substituted carbon), 43.6, and 42.8 ppm. These values are very similar to those reported for $[Co(1,4,7\text{-triazacyclononane})(dapo)Cl]^{2+}$ with N,N-coordinated dapo.[18]

Resolutions and Chiroptical Properties. The $(-)_{578}$ enantiomers of complex ions **1**–**3** were enriched by precipitation with $(-)_{546}$-dibenzoyl-L-tartaric acid, and from their mother liquors, their antipodes were further enriched by precipitation with dibenzoyl-D-tartaric acid. These precipitates had a very complex composition, and no substantial effort was made to establish their empirical formula. Constant ellipticities of $(+)_{578}$- and $(-)_{578}$-**1** and $(-)_{578}$-**2** were achieved by repeating the resolution procedure. The resolution of **3** was less efficient by this method. Therefore, partially resolved **1** was reacted with N_3^- to give **3** of higher optical purity after crystallization as the bromide. $(-)_{578}$-**3**-Br_2 was thus taken to be less soluble than the racemate and could be recrystallized to constant ellipticity. In another experiment, supposedly optically pure **1** was treated with N_3^- in the same way to give optically pure **3**.

Chemical correlations between the resolved species were then established with use of known stereoretentive reactions to check the optical purity of the products of constant ellipticity. The reactions used in the stereochemical cycles are shown in Scheme II. The results are consistent with ≥97% optical purity of the samples used or, alternatively, with ≥97% retention of configuration in the reactions carried out.

Solvolysis Kinetics. The solvolysis of **1** and **2** in acidic aqueous solution was followed spectrophotometrically at 310 nm (**1**) or at 370 nm (**2**). The reactions followed the usual rate law $v = -d[\text{complex}]/dt = k_{H_2O}[\text{complex}]$, with $k_{H_2O} = 1.0 \times 10^{-5}$ s^{-1} for **1** and 4.1×10^{-5} s^{-1} for **2** at 25 °C and 1 mol dm^{-3} $HClO_4$. The first of these rate constants is similar to $k_{H_2O} = 1.7 \times 10^{-5}$ s^{-1} found for $[Co(bamp)(tmd)Cl]^{2+}$ under these conditions, indicating but a minor influence of the OH function in dapo on the rate constant. The Hg^{2+}-induced aquation of **1** was measured at 25 °C and 310 nm ($[Co]_t = 3 \times 10^{-3}$ mol dm^{-3}; $[Hg^{2+}] = 3.13 \times 10^{-2}$ mol dm^{-3}; $[H^+] = 0.1$ mol dm^{-3}; $\mu = 1.05$, $NaClO_4$). If the same rate law for **1** as for $[Co(bamp)(tmd)Cl]^{2+}$ is assumed,[15] $k_{Hg} = 0.85$ dm^3 mol^{-1} s^{-1} for **1**. The tmd complex has $k_{Hg} = 1.4$ dm^3 mol^{-1} s^{-1} under these conditions, again indicating little influence from the OH function at dapo.

Table II. Base Hydrolysis Kinetics of $[Co(bamp)(dapo)X]^{2+}$ Complexes in Water at 25 °C

complex	pH	k_{obsd}, s^{-1}	k_{OH}, M^{-1} s^{-1} [f]
1 (X = Cl)[a]	8.65[b]	0.012	2700
	8.62[c]	0.012	2900
	8.47[b]	0.0078	2600
	8.53[d]	0.11	3200
	8.14[c]	0.0045	3300
	8.08[b]	0.0035	2900
	7.93[c]	0.0026	3100
		av	2960 ± 260
2 (X = Br)[e]	8.67[c]	0.073	1.5×10^4
	8.21[c]	0.024	1.5×10^4
	8.01[b]	0.020	1.9×10^4
		av	$1.6 \pm 0.2 \times 10^4$

[a] Monitoring wavelength, 310 nm; $[Co]_t = 6 \times 10^{-4}$ mol dm^{-3}. [b] Triethanolamine–$HClO_4$ buffer; $[B]_t = 0.1$ mol dm^{-3}; $\mu = 1.0$ ($NaClO_4$). [c] "Tris"-$HClO_4$ buffer; $[B]_t = 0.1$ mol dm^{-3}; $\mu = 1.0$ ($NaClO_4$). [d] Triethanolamine–$HClO_4$ buffer; $[B]_t = 0.1$ mol dm^{-3}, $\mu = 1.0$ ($NaClO_4$); $[Co]_t = (5–6) \times 10^{-3}$ mol dm^{-3}. [e] Monitoring wavelength, 360 nm; $[Co]_t = 4.8 \times 10^{-3}$ mol dm^{-3}. [f] $k_{OH} = k_{obsd}/[OH^-]$, based on $pK_w = 14.00$.

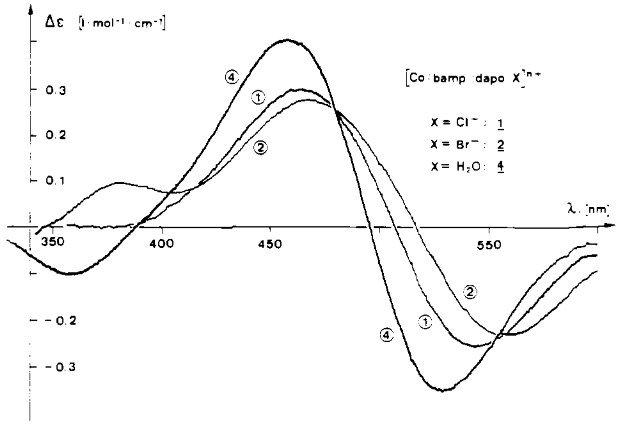


Figure 3. CD spectra in 0.1 mol dm^{-3} $HClO_4$.

The base hydrolysis reactions of **1** and **2** were studied (Table II) in buffer solutions (pH 7.9–8.6). The usual rate law $v = k_{OH}[\text{complex}][OH^-]$ was observed. There is no general base catalysis term as k_{OH} is essentially constant for different buffer base concentrations.

Stereochemistry of Base Hydrolysis. Samples of optically pure $(-)_{578}$-**1** and $(-)_{578}$-**2** were base hydrolyzed for $10 \times t_{1/2}$. The CD spectra of the acidified reaction solutions were then compared with those obtained after Hg^{2+}-induced aquation of the same reactants. Great care had to be taken to accurately match the medium in which all four CD spectra were recorded.[20] All four spectra were identical within the error (Figure 3); thus ≥98% retention of configuration obtains in the base hydrolysis reaction, i.e., full retention within the error.

Competition Experiments with Azide Ion. When the base hydrolysis reaction in the presence of 1 mol dm^{-3} N_3^- was carried out, formation of azido complex **3** was observed in analogy to other Co(III) pentaamines (Table III). Two uncommon difficulties arose. Firstly, the material balance was incomplete after elution of the azido and aqua (**4**) complexes from the ion-exchange resin. An orange zone remained at the top of the resin that could not be eluted even with 10 mol dm^{-3}

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(18) Okamoto, M. S.; Barefield, E. K. *Inorg. Chim. Acta* **1976**, *17*, 91.

(19) Remar, J. F.; Pennington, D. E.; Haim, A. *Inorg. Chem.* **1965**, *4*, 1832.

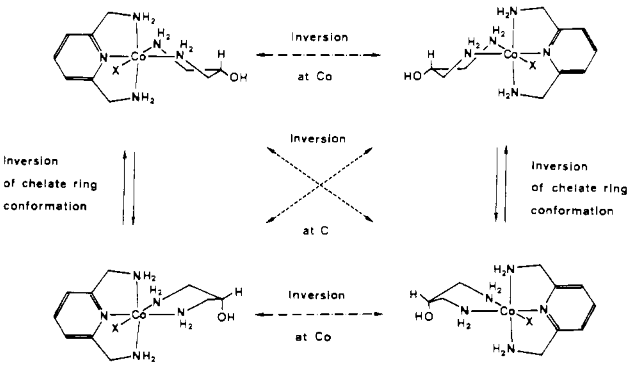
(20) E.g., with no added Hg^{2+} to the acidified base hydrolysis reaction solution, the CD spectrum qualitatively agreed, but the intensity in that medium suggested 16% racemization. This medium effect vanishes upon addition of the corresponding amount of Hg^{2+}. A similar observation was made in the nitrosation reaction.

Table III. Competition Experiments in 1 M N_3^- in Aqueous Solution at 25 °C

complex	% hydroxo prod.	% azido prod.	% unknown prod.	no. of determins	ref
$[Co(bamp)(dapo)Cl]^{2+}$	82.5 ± 0.5	6.5 ± 0.5[a]	11 ± 1[b]	3[c]	this work
$[Co(bamp)(dapo)Br]^{2+}$	83 ± 1	6 ± 1[a]	11 ± 2[b]	2[c]	this work
$[Co(bamp)(tmd)Cl]^{2+}$	92	8	...		22
$[Co(bamp)(tmd)Br]^{2+}$	91	9	...		22
$[Co(bamp)(en)Cl]^{2+}$	91	9	...		22
[*cis*-$Co(en)_2NH_3Cl^{2+}$][d]	76 ± 1	24 ± 1			5
[*trans*-$Co(en)_2NH_3Cl^{2+}$][d]	74 ± 1	26 ± 1			5
$[(H_3N)_5CoCl^{2+}]$[d]	90.5 ± 1.0	9.5 ± 1.0			6

[a] Of these quantities, $\lesssim 2\%$ arise from subsequent reaction of the hydroxo product with N_3^-. [b] Determined by difference only; 100% recovery of hydroxy and azido products assumed. [c] Experiments using optically pure reactants gave optically pure hydroxo and azido products. [d] Results agree within the experimental error for the leaving groups other than Cl^-, e.g., Br^-, NO_3^-.

Scheme III. Configurational and Conformational Interrelations in $[Co(bamp)(dapo)X]^{2+}$ Ions



hydrochloric acid.[21] However, this product was not formed in the absence of azide under otherwise identical conditions, and the hydroxo complex was quantitatively formed and recovered as the aqua ion after ion exchange. No analogous unknown product was detected in the reactions of $[Co(bamp)(tmd)Cl]^{2+}$ and $[Co(bamp)(en)Cl]^{2+}$ under the same conditions.[22]

Secondly, $[Co(bamp)(dapo)OH]^{2+}$ was found to react with azide ion at such a rate that the amount of **3** measurably increased when the base hydrolysis reaction was carried beyond <3 half-lives. Preliminary kinetics using the hydroxo complex as the limiting reagent showed that this process is not a uniphasic, first-order reaction. The initial rates depended on $[OH^-]$ at pH 9.7–11.1 where no contribution from the conjugate aqua ion is expected. This complicating feature was not studied further, but interference from this source was minimized to ≤2%; thus at least 3–4% of the azido complex must arise from competition, independent of whether the leaving group is Cl^- or Br^-. On the other hand, no N_3^- anation of $[Co(bamp)(tmd)OH]^{2+}$ or $[Co(bamp)(en)OH]^{2+}$ was observed on the time scale of the competition experiments.[22]

Discussion

Configuration of $[Co(bamp)(dapo)X]^{2+}$ Complexes. The spectral data support the proposed structure with N,N′-coordinated dapo (Figure 1). For describing the handedness of these complex ions, it is practicable to define an axis of chirality that passes through the OH-substituted carbon and the Co atom, bisecting the N(pyridine)–Co–Cl angle. The chirality would then be defined on the basis of the orientations of the Cl and N(pyridine) atoms bound to cobalt and of the H and OH substituents at the central dapo carbon atom. Application of the pertinent sequence rule[23] leads to *S* chirality for the enantiomer drawn in Figure 1. This type of axial chirality resulting from combination of a ligand-based prochiral center with a prochiral, octahedral fragment appears uncommon. The standard helicities Δ,Λ[24] are not defined for these complex ions as the two possible skew pairs cancel out. This unusual situation also precludes attributing unambiguously the considerable CD intensity of these complexes to one of the classical sources (configurational, conformational, and vicinal effects[25]).

A more detailed discussion of the chiroptical properties is referred to a later communication that will include X-ray structure data for **3**.[22] The configurational aspects are summarized in Scheme III, which emphasizes the mutual dependence of the two possible centers of chirality (central carbon of dapo and Co) and the conformational interconversions in the limiting chair conformations of the six-membered chelate ring.

The Base Hydrolysis Mechanism. The kinetic data (Table II) are consistent with "normal" pentaamine reactivity, i.e., **1** reacts neither unusually faster nor slower than $[Co(bamp)(tmd)Cl]^{2+}$.[15] Therefore, the dapo hydroxyl group does not appear to appreciably influence the reactivity. As the structurally similar complex $[Co(bamp)(tmd)Cl]^{2+}$ has an amine proton exchange pattern characteristic of "normal" Co(III) pentaamines,[15] we may assume the usually proposed[2-4] mechanism of activation of the leaving group. While all features of these new complexes are fully consistent with a conjugate base mechanism, little can be said with certainty about the site of deprotonation. Both trans[14,26] and cis[12,13,27] deprotonation has been suggested, and the importance of secondary amine protons in the activation process has been emphasized.[13,28] **1** and $[Co(bamp)(tmd)Cl]^{2+}$ have no such proton, and their averaged reactivity lies about halfway in between those of *mer* and *fac* isomers of $[Co(dien)(tmd)Cl]^{2+}$,[28] the *mer* isomer being >100 times more reactive than the bamp complexes. Two major factors must be considered to explain this difference: high acidity of the secondary amine proton and enhanced reactivity of the corresponding conjugate base. NH proton-exchange rates (as a measure of the relative acidities[13,26]) are not available for *mer*-$[Co(dien)(tmd)Cl]^{2+}$, but the analogous "planar" secondary amine functions in $[Co(trien)(glyO)]^{2+}$ [29,30] and in [Co(*sym*-trenen)Cl]$^{2+}$ [14] do

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(21) This material was shown to contain cobalt by X-ray fluorescence analysis, but reliable determination of these small amounts of metal proved very difficult with or without destruction of the resin.

(22) Tinner, U. Thesis, E.T.H., No. 6463, aku-Fotodruck, Zürich, 1979.

(23) Cahn, R. S.; Ingold, Ch.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(24) *Inorg. Chem.* **1970**, *9*, 1.

(25) Hawkins, C. J. "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1971; pp 175–227.

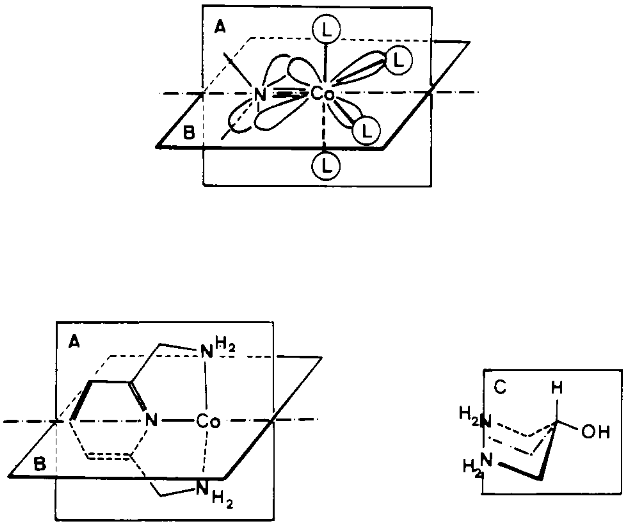
(26) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M. *Inorg. Chem.* **1975**, *14*, 1485.

(27) Buckingham, D. A.; Marty, W.; Sargeson, A. M. *Helv. Chim. Acta* **1978**, *61*, 2223.

(28) Dong, L. S.; Gainsford, R. A.; House, D. A. *Inorg. Chim. Acta* **1978**, *30*, 271.

(29) Buckingham, D. A.; Cresswell, P. J.; Dellaca, R. J.; Dwyer, M.; Gainsford, G. J.; Marzilli, L. G.; Maxwell, I. E.; Robinson, W. T.; Sargeson, A. M.; Turnbull, K. R. *J. Am. Chem. Soc.* **1974**, *96*, 1713.

Chart I. Symmetry Criteria for π Stabilization and the Construction Principle in $[Co(bamp)(dapo)X]^{n+}$ Ions

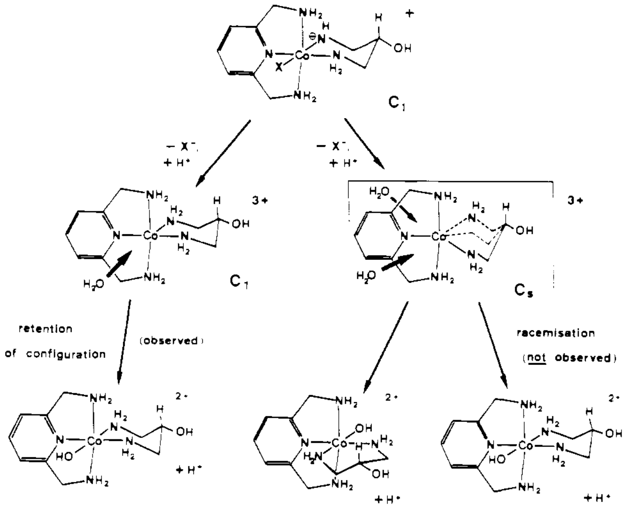


exchange protons some $10-10^3$ times faster than all other amine functions. If this regularity extends to the dien complexes, then most, if not all, of the decrease in rate for the bamp complexes is accounted for and no special assumptions on the reactivity of the conjugate base need be made.

Anion competition experiments[5,6] to test for the existence of a common, leaving-group-independent intermediate state in these substitutions have become a standard procedure. Such experiments on the $[Co(bamp)(dapo)X]^{2+}$ species were hampered by the formation of a new species, which tenaciously resisted elucidation of its nature. The complex ions **1** and **2** are therefore not suitable for detailed mechanistic study of this type. We note, however, that such species are formed neither in the absence of azide nor with $[Co(bamp)(tmd)Cl]^{2+}$ as the starting material. Clearly it is not a product arising from secondary reaction of the azido complex. Moreover, it is formed in essentially equal amounts from the chloro and bromo complexes. The percentage of anion competition is subject to an unusually large error due to relatively rapid reaction of the hydroxo product with azide ion. This process does not have its origin in the unknown product, for it is also observed in its absence. The amount of azido complex that arises from **1** and **2** by competition for an intermediate state agrees within the (unusually broad) limits of error, and thus the present results at least do not reveal a leaving-group dependence.[31]

Considering the structural similarity between $[Co(bamp)(dapo)X]^{2+}$ and $[Co(bamp)(tmd)X]^{2+}$ ions, it seems appropriate to include in this discussion the preliminary competition results available for the latter (Table III). Since the amounts of azide scavenging are small, minor leaving-group dependence (as has been observed recently for other systems[8-10]) is not easily detected. Such leaving-group dependence is inconsistent with a S_N1 (lim) or D mechanism, and the data on this and previous systems[8-10] may be explained by an I_d or $S_N1(cB)IP$[10b] mechanism where the molecular state reached by loss of the leaving group is not long-lived enough to equilibrate with its environment before the incoming ligand enters the first coordination sphere.

Scheme IV. Possible Stereochemical Pathways in Base Hydrolysis of $[Co(bamp)(dapo)X]^{2+}$ Ions[a]



[a] Deprotonation trans to the leaving group is an alternative possibility.

Stereochemistry of the Base Hydrolysis Reaction. We will first discuss the reasons for choosing the $[Co(bamp)(dapo)X]^{n+}$ system in an attempt at testing the π-stabilization hypothesis.[11] This choice is largely dictated by the maximum orbital overlap conditions in an optimally stabilized five-coordinate intermediate (Chart I). These suggest the use of a rigid tridentate ligand with two planes of symmetry. One of these (B) bisects the ligand so as to coincide with the main axis of the π-stabilizing central nitrogen orbital. All atoms of this ligand must lie on, or be symmetrically disposed relative to, the second plane (A), which is perpendicular to the first. The intersection of the two planes coincides with the axis Co–N(pyridine). Clearly, bamp meets these requirements provided the possible conformers of the coordinated ligand will equilibrate on the time scale envisaged. The bidentate ligand of our choice should, as soon as the complex has lost the leaving group, be able to accommodate an angle close to 120° without excessive strain, and dapo is expected to satisfy this condition in good approximation.

As in earlier studies,[5,6,8-10] structural features of the supposed intermediate are deduced from a structural comparison of the reactant with the product(s). Since in most cases two different five-coordinate polyhedra may be generated by rearrangement, viz., pentahedra (tetragonal pyramids)[32] and hexahedra (trigonal bipyramids),[32] the interpretation of observed configurational change remains ambiguous.[33] The backbone of bamp is rigid enough to prevent formation of rearranged pentahedral intermediates with a reduced area of the square-bottom face of the pentahedron.[37] In $[Co(bamp)(dapo)X]^{n+}$, only one mode of large-amplitude intramolecular motion has a reasonable chance to occur and will lead to hexahedral intermediates, which should give at least partial racemization. One of these intermediate states is unique in having the proper symmetry for π stabilization. The OH group of dapo serves as a stereochemical tag introducing chirality in the octahedral starting material (Scheme III) without destroying the plane of symmetry ($A \equiv C$) in the π-stabilized intermediate under consideration. If this intermediate is formed, then attack of solvent of other nucleophiles would lead to complete racemization (provided amine deprotonation does not interfere; see below), Scheme IV.

An important difference between the present pentaamine series and all those known previously is that the supposed π-stabilizing orbital is not generated by amine deprotonation.

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(30) Buckingham, D. A.; Dwyer, M.; Gainsford, G. J.; Janson Ho, V.; Marzilli, L. G.; Robinson, W. T.; Turnbull, K. R. *Inorg. Chem.* **1975**, *14*, 1739.

(31) Current work intends to circumvent these problems by replacing the dapo-OH by an "innocent" substituent.[22] dapo had been chosen because it allows chemical variation by reactions at the coordinated ligand.

(32) Britton, D.; Dunitz, J. D. *Acta Crystallogr., Sect. A* **1973**, *A29*, 362.

(33) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5129; **1968**, *90*, 6539.

In fact, neither the bamp nor the dapo deprotonated nitrogen p orbitals can meet the requirements for significant π-stabilization although all four could, in principle, provide the reactive conjugate base. A conjugate base with deprotonated bamp–NH_2 cannot lead to the rearranged intermediate state for π-stabilization, and the main axis of the p orbital on deprotonated dapo–NH_2 cannot be aligned without a major increase in strain with the trigonal plane of a π-stabilized intermediate state. This last possibility would therefore at best provide a small part of the maximum π stabilization and would lead to the same stereochemical consequences as π stabilization via the pyridine π orbital, provided no dissymmetry is introduced by the site of deprotonation during entry of the new ligand (see below). However, the anticipated stereochemical consequence, resulting from either of these two possibilities for π stabilization, viz. racemization, is not observed. Certainly the lifetime of the coordinatively unsaturated intermediate state arising from loss of the leaving group is not lengthened appreciably by such bonding.

The observed retention of configuration in base hydrolysis may be interpreted in different ways:

(1) Since the anion competition results hint at a very short-lived intermediate state after loss of the leaving group (which appears to be shorter lived than equilibration of the second coordination sphere with the bulk solvent), one could view the stereoretentive course of the reaction as caused by a directing effect of the deprotonated nitrogen on the incoming nucleophiles. If the attacking nucleophile is water, then its entering may be concerted with protonation of the conjugate base, i.e., the reprotonating water molecule enters the coordination sphere in the proximity of the deprotonated amine function. If the site of deprotonation is the dapo–NH_2 function cis to the leaving group (as postulated in Nordmeyer's stereochemical analysis[12]), then full retention of configuration is possible under these particular circumstances even if the intermediate state has become a trigonal bipyramid by rearrangement. However azide scavenging cannot be concerted with reprotonation in our experiments, and since the azido complex is formed with full retention of configuration, we may dismiss this first interpretation.

(2) The pyridine π-orbital system may be too poor a donor to make enough π bonding to stabilize a symmetric trigonal-bipyramidal intermediate. In addition, an undistorted square-pyramidal intermediate has the proper symmetry for stabilization by [$3d_{xy}(Co) \rightarrow \pi^*$(pyridine)] back-bonding.

While no evidence for such bonding has been found in a ^1H and ^{13}C NMR study,[34] there is ligand field spectral evidence for it in $Co(bpy)_3^{3+}$,[35] $Co(phen)_3^{3+}$,[35] and $Co(py)_4X_2^{+}$[36] complexes. For symmetry reasons, it is also favorable in a five-coordinate intermediate state of undistorted square-pyramidal geometry. This bonding would be weakened by rearrangement into a trigonal-bipyramidal state since under ideal D_{3h} symmetry, the orbitals $3d_{xz}$ and $3d_{x^2-y^2}$ are degenerate, leaving the donating metal orbital incompletely occupied. Similar arguments are pertinent to our system where a trigonal bipyramid of C_s symmetry may be attained. As a consequence, the presumably weak π-stabilization effect in the trigonal-bipyramidal state may be outweighed by the back-bonding effect in the square-pyramidal state, leaving the intermediate a square pyramid throughout its lifetime.

Conclusion

In the base hydrolysis experiment described here, the π-orbital system of a pyridine nucleus is coordinated to a Co(III) center in such a way that π-orbital overlap [$2p(N(\text{pyridine})) \rightarrow 3d_{x^2-y^2}(Co(III))$] could have developed during loss of the leaving group without the necessity of change in the relative orientation of Co and pyridine during rearrangement of the coordinatively unsaturated intermediate state toward hexahedral geometry. Such bonding has defined and observable stereochemical consequences that are not observed. Only marginal possibilities for π stabilization are anticipated for the coordinated NH_2 functions in the reactant. Since the typical rate acceleration in base hydrolysis is observed, it is suggested that possibilities of stabilizing the coordinatively unsaturated intermediate state other than π bonding exist although their nature cannot be deduced reliably from these experiments.

Acknowledgments. This work has been supported by the Swiss National Foundation for Scientific Research (Projects 2.225-0.74 and 2.817-0.77). We thank Dr. K. L. Loening, Chemical Abstracts Service, Columbus, Ohio, for advice on the nomenclature in this paper and Professor C. E. Schäffer, H. C. Ørsted Institute, Copenhagen, for discussion and communication of results prior to publication.

Registry No. **1**-$(ClO_4)_2$, 78625-00-0; $(-)_{578}$-**1**-$(ClO_4)_2$, 78624-90-5; $(+)_{578}$-**1**-$(ClO_4)_2$, 78624-92-7; **2**-$ZnBr_4$, 78683-96-2; $(-)_{578}$-**2**-$ZnBr_4$, 78624-94-9; $(+)_{578}$-**2**-$ZnBr_4$, 78624-96-1; **3**-$ZnCl_4$, 78683-98-4; $(-)_{578}$-**3**-Br_2, 78624-97-2; $(-)_{578}$-**4**, 78624-98-3.

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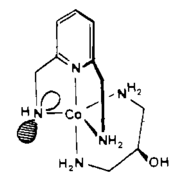
(34) Lavallee, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718.

(35) Josephsen, J.; Schäffer, C. E. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 813.

(36) Laier, T.; Schäffer, C. E.; Springborg, J., unpublished work; *Acta Chem. Scand., Ser. A* **1980**, *34*, 343.

(37) One reviewer argues that the intermediate



could accommodate the results. This structure would appear *at least* as strongly strained as one with a dapo–NH_2 p orbital properly oriented for π bonding.